

Engineer Technical  
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Engineering and Design  
MEASUREMENT OF DISSOLVED GASES TO  
DETERMINE THE DEGREE OF NITROGEN  
SUPERSATURATION

1. Purpose. The purpose of this letter is to provide information on the types of in situ and laboratory methods available to measure dissolved gases in rivers and reservoirs. Information is also provided to help select locations for in situ measurement and proper techniques for sample collection and preservation.

2. Applicability. This letter applies to all field operating activities having Civil Works responsibilities.

3. Reference and Bibliography.

a. References.

(1) ER 15-2-10. Committee on Water Quality.

(2) ETL 1110-2-239. Nitrogen Supersaturation.

b. Bibliography.

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(4) D'Aoust, B.G., R. White and H. Seibold, 1976. An Electronic Monitor for Total Dissolved Gas Pressure. Proceedings of the Workshop on Gas Bubble Disease, (Richland, Washington, October 8-9, 1974) pp. 106-110.

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(6) Garton, R.R., H.A. Salman, and F.C. Heller, 1973, Western Proceedings, Western Assoc. of State Game and Fish Commissioners. (Salt Lake City, Utah. July 11-13, 1973.) 53:492-514.

- (7) Lange's Handbook of Chemistry, 1979, 12th Edition, McGraw-Hill Company, New York, N.Y.
- (8) Lee, G.F. and P.H. Martin, 1975, Water Research 9:643-648.
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- (11) Standard Methods for the Examination of Water and Wastewater, 1975, American Public Health Association, 14th Edition, APHA-AWWA-WPCF, Washington, D.C.
- (12) Swinnerton, J.W., V.J. Linnenbom and C.H. Cheek, 1962, Analytical Chemistry, 34:483-485, 1509.
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#### 4. Statement of Problem.

a. Supersaturation of atmospheric gases has been identified as a potential environmental problem associated with releases from certain Corps impoundment projects. This supersaturated condition can develop when the flow experiences significant changes in pressure and temperature as it passes through a spillway or outlet works and an energy dissipating structure.

b. Most incidents of supersaturation have been observed downstream of a spillway discharging into a highly submerged (deep) stilling basin. In general, hydropower turbines have not been associated with this problem. However, Garton et al. (1973), found that supersaturated levels up to 130 percent were produced at times below turbines. Another source of supersaturation is the discharge of cooling water, particularly from thermal power generation (Lee and Martin, 1975). This condition results from the lowering of solubility of all gases in water as the water temperature increases.

c. Spillway operation can induce supersaturation when air, entrained as small bubbles, is trapped in the water as it flows down the spillway. This air is forced into solution by the hydrodynamic pressure developed in the flow as it plunges into and passes through the stilling basin. The dissolved gas content can be increased to levels exceeding saturation with respect to the surface. When this water flows downstream, it can remain supersaturated for long distances. The rate of equilibration with the atmosphere in the normal river environment is dependent on the

26 Sep 80

d. Fish mortality attributed to this gas problem has been experienced in the North Pacific Division and downstream of the partially completed Harry S. Truman project in the Missouri River Division. These incidents of fish mortality were found to result from gas bubble disease which is caused by subjecting fish to prolonged periods of gas supersaturation.

## 5. Gas Solubility.

a. The equilibrium solubility of gases in fresh water is dependent on two factors; the water temperature and the partial pressure of the gas in equilibrium with the liquid. The solubility of all gases in water declines with increasing temperature. Thus water that is saturated with a gas, when warmed quickly, can become supersaturated. This can result in a problem when cooling water is discharged from thermal power generating stations. On the other hand, water supersaturated with gas can often be brought to a saturated or sub-saturated condition by cooling. This is important for preservation and transport of samples for analysis.

b. The dependence of gas solubility on the partial pressure of the gas in equilibrium with the liquid is described by Henry's law (Castellan, 1964).

$$X_i = \frac{1}{K_i} p_i$$

where  $X_i$  is the mole fraction of the gas "i" in solution (solubility),  $K_i$  is the Henry's law constant for substance "i" at a given temperature, and  $p_i$  is the partial pressure of the gas "i" (in atmospheres) in equilibrium with the liquid.

c. Alternatively, Henry's Law can be expressed using a volumetric solubility coefficient  $a_i$  (or  $B_i$  in Weiss papers) as:

$$C_i = P_i a_i$$

where  $C_i$  is the concentration of gas "i" in of dry gas at standard temperature and pressure (STP),  $P_i$  is the partial pressure of gas "i" in atmospheres and  $a_i$  is the Bunsen solubility coefficient of gas "i" in dry gas at STP per solution at the equilibrium temperature. It should be emphasized that  $P_i$  is the total partial pressure of the gas "i." At the water surface,  $P_i$  is the atmospheric pressure minus the water vapor pressure at that temperature times the percentage of that gas in the atmosphere. The percentage composition of nitrogen in the atmosphere is about 78 percent. Thus, the partial pressure of nitrogen

26 Sep 80

at a dry atmospheric pressure of 1 atmosphere (760 torr) neglecting water vapor would be 1.0 times 0.78 or 0.78 atmospheres (592 torr).

d. When one considers the gas phase or bubble at depth, however, it is necessary to add the hydrostatic pressure of the water column to obtain the partial pressure of the gas in the bubble. For example, in fresh water at a depth of 34 feet, the hydrostatic pressure of the water column is approximately one atmosphere. The water at this depth is thus subjected to a total pressure of about two atmospheres and the gas phase at this depth is under a partial pressure of nitrogen of 1.56 atmospheres ( $2 \times 0.78$ ) assuming the water is in equilibrium and the surface partial pressure of nitrogen is 0.78 atmospheres. Since the Henry's law constant is to a first approximation independent of pressure, the equilibrium solubility of nitrogen at 34 feet is therefore expected to be about twice that at the surface.

e. The presence of salts in water decreases gas solubility. However, unless highly saline water is being analysed (salinity in excess of 5 parts per thousand), this effect is small and can be neglected. Solubility tables which include the effect of salinity are available in Weiss (1970).

## 6. Measurement Methods.

a. Two devices are commercially available to measure dissolved gas concentrations in the field. The gas saturometer appears to be the most reliable, but has the disadvantage of being limited to surface measurements. The gas tensionometer is more versatile in that it can be used to obtain measurements at depth. Experience suggests, however, that the electronic components of the tensionometer require more care and service. Appendix A contains a further description of these devices.

b. Calibration of the saturometer or tensionometer and verification of measurements are difficult. Obviously, standard solutions for calibration do not exist nor would such a concept be practicable. Calibration can only be accomplished indirectly by obtaining a measurement in a free flowing stream and simultaneously collecting a sample for laboratory analysis. This should be accomplished prior to any data collection effort.

c. To maintain confidence in the accuracy of the measurements, two saturometers or a saturometer and a tensionometer should be employed in the field. The two units, submerged side-by-side, should provide essentially the same value. If a difference is observed between two saturometers, the one with the lower value will generally be in error. However, a difference between a saturometer and a tensionometer, or between two tensionometers, points out that a problem exists, but will not identify the unit in error. One or more samples, the number depending on the complexity of the stream, should be collected for

26 Sep 80

laboratory analysis during each field exercise. Analysis of these samples will provide verification of the data obtained with the field equipment. Section 8 contains a discussion of the problems and procedures associated with sample collection and handling.

d. Several procedures are available for laboratory analysis. These include gas chromatographs, mass spectrometers, and the Van Slyke method. A limited description of the laboratory techniques is found in Appendix B. Gas Chromatographic (GC) analysis should be readily available, more accurate, and the least expensive of the laboratory procedures. A portable gas chromatograph has been used by personnel of CRREL and the Hydraulics Laboratory, WES, but should be considered for field office use at this time.

7. Sampling Location. Whether in situ or laboratory methods are chosen for analysis, the most critical factor in obtaining good dissolved gas data is the choice of sampling location. None of the in situ or laboratory methods available are capable of accurately measuring dissolved gases when free gas bubbles are present. It is therefore desirable to choose a site where bubbles are not visible in the water. At any potential site, a sample of the water should be collected and visually inspected before the site is accepted. The chosen site will typically be at least several hundred meters downstream of any structure or "whitewater" and may in some cases be considerably further downstream. Multiple measurement stations will be required to adequately define the lateral distributions and vertical profiles of dissolved gases since many streams will not be fully mixed at the sampling cross section.

#### 8. Sample Collection and Handling for Laboratory Analysis.

a. Samples collected for laboratory analysis should be obtained at the same depth and simultaneously with a reading of the field instrument. The sampling tube (Kemmerer or Van Dorn) should be cooled to a temperature equal to or less than the temperature of the water to be collected. This can be easily accomplished by hanging the tube at the sampling depth long enough to cool, pulling it to the surface to purge the encased water, then lowering it to the sampling depth again to obtain the sample. When the sample is brought to the surface, it should be inspected for bubbles. If bubbles are present or are formed when the sample is transferred, it should be discarded and another sample obtained.

b. Two methods are available for shipping the sample to the laboratory. The sample can be carefully poured into a cold BOD bottle and transported to the laboratory at temperatures just above freezing. This method is the best choice if analysis is to be performed by GC with a Swinnerton stripping chamber. If the sample freezes, it is unuseable. If it warms during transport and vibration causes bubbles to form, the sample must be discarded. Furthermore, the sample should be analyzed within 24 hours after reaching the laboratory. Another alternative is

26 Sep 80

shipment of the samples in 50 gas-tight syringes. This method has the advantage that any bubbles that form are retained within the syringe. Thus bubble formation does not necessarily indicate that the sample must be discarded. If this procedure is chosen, the syringes should be filled to overflowing, the plunger inserted and water expelled through the needle until 25 remains. The remaining 25 should be filled with helium either in the field or once the samples arrive at the laboratory. This procedure is best suited to the headspace analysis method used in conjunction with GC.

9. Recommendations. The Nitrogen Supersaturation Work Group of the Corps Committee on Water Quality (ER 15-2-10) evaluated the options available for measurements of dissolved gas concentrations on site and in the laboratory. If temperature and dissolved oxygen measurements indicate that the stream is vertically mixed, the satumeter is the recommended device for field measurement. However, if the temperature and dissolved oxygen measurements change with depth, the tensionometer should be used, but with caution because it has not been fully field tested. The accuracy of either device should be determined before field measurements are taken. Furthermore, confidence in the field measurements can be maintained only if one or more samples are collected each day of the field exercise for laboratory analysis. It is recommended that laboratory analysis be conducted by GC equipped with a Swinnerton stripping chamber. In most cases, it will be necessary to have these analyses performed by a commercial laboratory. Determine beforehand that the selected laboratory is capable of performing the analysis and that the appropriate quality control procedures are enforced.

10. Additional Information. Should further information be needed contact members of the Corps of Engineers Committee on Water Quality (ER 15-2-10).

FOR THE CHIEF OF ENGINEERS:



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4 Appendixes

App A - In Situ Methods

App B - Laboratory Methods

App C - Carbon Dioxide

Considerations

App D - Gas Solubility Tables